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Infrared spectroscopy and microwave dielectric properties of ultra-low temperature firing $(K_{0.5}La_{0.5})MoO_4$ ceramics

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ABSTRACT

The $(K_{0.5}La_{0.5})MoO_4$ ceramics with intrinsic ultra-low sintering temperature were prepared via the solid state reaction method. Pure monoclinic $(K_{0.5}La_{0.5})MoO_4$ phase was formed at around 660 °C. High performance of microwave dielectric properties were obtained in ceramic sample sintered at 680 °C with a permittivity of ~10.3, a temperature coefficient of resonant frequency about −81 ppm/°C, and Qf value of 59,000 GHz. Complex dielectric spectra gained from the infrared spectra were extrapolated down to microwave range, and they were in good agreement with the measured microwave permittivity and dielectric losses. The novel $(K_{0.5}La_{0.5})MoO_4$ ceramic might be a good candidate for microwave devices application.

1. Introduction

With the fast development of mobile communication, satellite communication, global position system (GPS), and other communication technologies, low temperature firing microwave dielectric ceramic materials have attracted much attention due to its use in low temperature co-fired ceramic (LTCC) technology, which becomes an important method because of its predominance in enabling fabrication of three-dimensional ceramic modules with low dielectric loss and cofired metal electrodes. Hence, search for microwave dielectric ceramic materials with wide range of dielectric permittivity (ε_r), high quality factor (Qf value), near zero temperature coefficient of resonant frequency (τ_f), and lower sintering temperature (S.T.) has been worked on all over the world.[1–3]

Recently, many Mo-based microwave dielectric ceramics with intrinsic low sintering temperatures have attracted much attention, such as $Bi_2Mo_2O_9$ [4], Li_2MoO_4 [5], $Li_2Zn_2Mo_3O_{12}$ [6], etc. Zhou et al.'s recent work showed that the $(K_{0.5}Nd_{0.5})MoO_4$ ceramic sintered at 760 °C for 2 h had good microwave dielectric properties [7]. The La ion has similar physical and chemical properties to the Nd ion and they can usually be substituted by each other to improve the properties of the compound, for example, $Ca(La_{1-x}Nd_x)_4Ti_4O_{15}$ [8], $(La_{1-x}Nb_x)BO_3$ [9], and $Ln_2Mo_3O_{12}$ (Ln=La, Nd) [10]. The $(K_{0.5}La_{0.5})MoO_4$ is an interesting host material for luminescent rare earth ions, and solid state laser media [11,12]. However, there has been no report on its microwave dielectric properties so far. Hence, the microwave dielectric properties and infrared spectroscopy of $(K_{0.5}La_{0.5})MoO_4$ were studied in the present work.

2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of K_2CO_3 (>99%, Guo-Yao Co, Ltd, Shanghai, China), La_2O_3 (>99%, Guo-Yao Co, Ltd, Shanghai, China) and MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) were prepared according to $(K_{0.5}La_{0.5})MoO_4$ composition. Powders were mixed and milled for 4 h. The mixed oxides were then calcined at 600 °C for 4 h. After being re-milled for 5 h, powders were pressed into cylinders in a steel die under a uniaxial pressure of 20 KN/cm^2. Samples were sintered at 660–720 °C for 2 h.

The crystalline structures were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surface with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). Microwave dielectric properties were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency (τ_f value) was calculated with the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85-25)} \times 10^6 \qquad (1)$$

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where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively. The Infrared (IR) reflectivity spectra were measured between 50 and 1500 cm^{-1} by a Fourier transform IR (FTIR) spectrometer (IFS 66v/S Vacuum, Bruker Optik Gmbh, Germany).

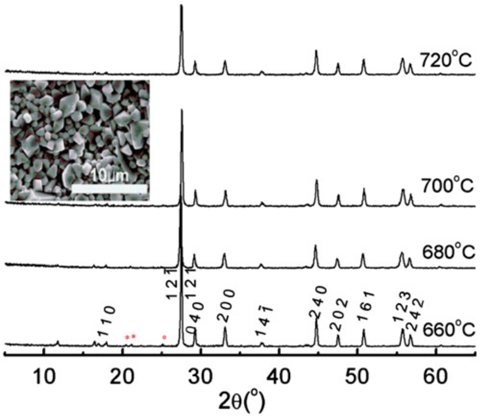

Fig. 1. X-ray diffraction patterns of the $(K_{0.5}La_{0.5})MoO_4$ ceramics sintered at different temperatures and SEM photograph of as-fired surface for $(K_{0.5}La_{0.5})MoO_4$ ceramic sintered at 700 °C (the inset part).

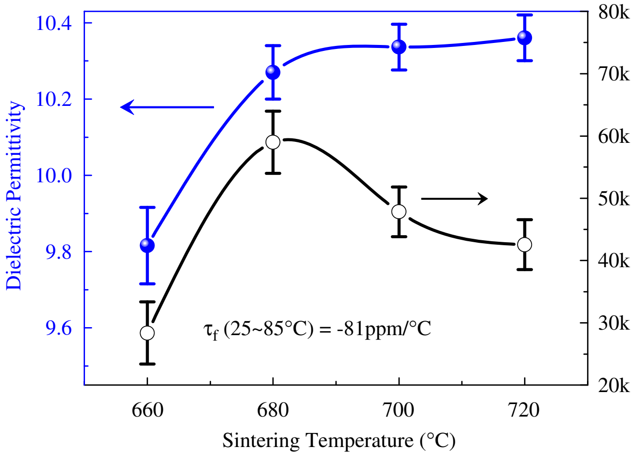

Fig. 2. Microwave dielectric permittivity and Qf values of $(K_{0.5}La_{0.5})MoO_4$ ceramic as a function of sintering temperature.

3. Results and discussion

The X-ray diffraction patterns of the $(K_{0.5}La_{0.5})MoO_4$ ceramics calcined and sintered at different temperatures are shown in Fig. 1. It is seen that the main phase of α-$(K_{0.5}La_{0.5})MoO_4$ was formed in sample sintered at 660 °C, in which a little unknown phase can be revealed. The peaks can be well indexed as a monoclinic structure, which agreed well with the result reported by Potapova et al. [13]. The α-$(K_{0.5}La_{0.5})MoO_4$ phase keeps stable even when the sintering temperature increased to 720 °C.

The SEM photograph of $(K_{0.5}La_{0.5})MoO_4$ ceramic sintered at 700 °C for 2 h is shown in the inset part of Fig. 1. Dense and homogeneous microstructure with almost no pores can be revealed. The grain size scattered in the range of 1–3 μm and the grains took on an octahedron shape, which might be related to its monoclinic crystalline structure. The density of $(K_{0.5}La_{0.5})MoO_4$ ceramic sintered at 700 °C is 2.320 g/cm^3.

The microwave dielectric permittivity and Qf values of $(K_{0.5}La_{0.5})MoO_4$ ceramic as a function of sintering temperature are shown in Fig. 2. It is seen that the dielectric permittivity increased sharply from 9.8 to about 10.3 as sintering temperature increased from 660 to 680 °C, which was caused by the elimination of pores with the increasing of sintering temperature, and then reached saturation in the temperature range 680–720 °C. The Qf value reached a maximum value about 59,000 GHz at the sintering temperature 680 °C. With the further increase of sintering temperature, the Qf decreased sharply due to the secondary grain growth. The calculated τ_f value from Eq. (1) is about −81 ppm/°C.

Fig. 3(a) presents the IR reflectivity spectra of $(K_{0.5}La_{0.5})MoO_4$ ceramic. The spectra were analyzed using a classical harmonic oscillator model. In this model the complex dielectric permittivity is written as

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - i\gamma_i\omega} \tag{2}$$

where $\varepsilon^*(\omega)$ is complex permittivity; γ_j, ω_{oj} and ω_{pj} are the damping factor, the transverse frequency and oscillator strength of the j-th Lorentz oscillator, respectively. The high-frequency permittivity ε_∞ results from electronic absorption processes much above the phonon frequencies; n is the number of transverse phonon modes. The complex reflectivity $R(\omega)$ can be written as:

$$R(\omega) = \left| \frac{1 - \sqrt{\varepsilon^*(\omega)}}{1 + \sqrt{\varepsilon^*(\omega)}} \right|^2 \tag{3}$$

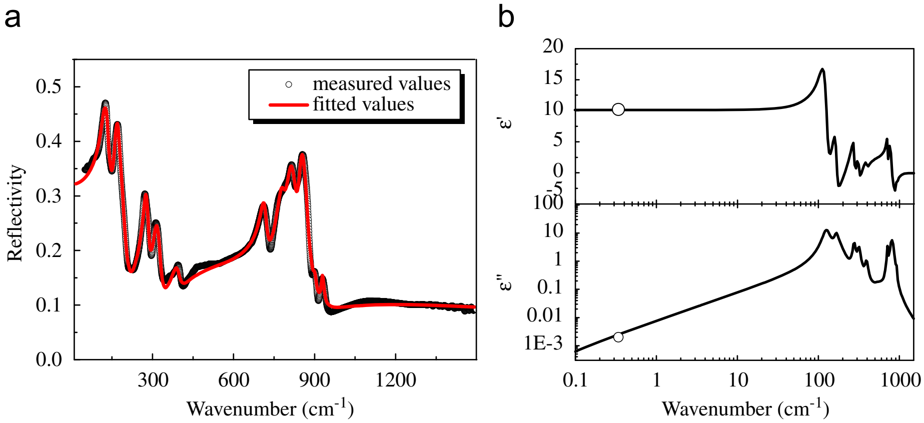

Fig. 3. The measured and fitted values of IR reflectivity spectra of $(K_{0.5}La_{0.5})MoO_4$ ceramic (a) and the calculated complex permittivity ε′ and ε″ (the circles present the measured values) (b).

The fitted IR reflectivity spectra and complex permittivity values are shown in Fig. 3(a) and (b), respectively. The extrapolated permittivity and dielectric loss from the fitted complex permittivity values (at around 10 GHz) of $(K_{0.5}La_{0.5})MoO_4$ are 10.1 and 0.0002, respectively. The results agree well with the measured values showed in Fig. 2. Hence, It can be deduced that the most polarization contribution for $(K_{0.5}La_{0.5})MoO_4$ ceramic at microwave region was attributed to the absorptions of phonon oscillation at infrared region.

4. Conclusions

The pure monoclinic $(K_{0.5}La_{0.5})MoO_4$ could be formed at about 660 °C and kept stable in the temperature range 660–720 °C. Dense $(K_{0.5}La_{0.5})MoO_4$ ceramic could be obtained in the sintering temperature 680–720 °C. The best microwave dielectric properties can be obtained in the ceramic samples sintered at 680 °C for 2 h with a permittivity 10.3, a τ_f value about -81 ppm/°C and Qf value 59,000 GHz. The IR reflectivity spectra were measured, and the fitted reflectivity spectra and complex permittivity values were obtained by employing Kramers–Kronig relationship. The extrapolated permittivity and dielectric loss from the fitted complex permittivity values agreed well with the measured values. The result means that the most polarization contribution for $(K_{0.5}La_{0.5})MoO_4$ ceramic at microwave region was attributed to the absorptions of phonon oscillation at infrared region.

Acknowledgments

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